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The Effect of Composition of Distillable Fractions on the Rheological Temperature Susceptibility of Cold Lake Asphalt

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Introduction

In another presentation (1) we proposed a model to explain the mechanisms in asphalt whereby changes in viscosity due to changes in temperature are resisted. In this work the rheological temperature susceptibilities of Cold Lake asphalt have been studied as components are distilled from it and then replaced with various amounts of materials of diverse nature, as well as mixtures of these materials. The results are explained on the basis of the model previously proposed.

Experimental

Distillation

Figure 1 shows the distillation conditions and fraction yields obtained from the distillation of Cold Lake asphalt. The temperature of the asphalt in the distillation flask was not allowed to exceed 340°C to avoid pyrolysis. Figure 2 shows the change in penetration values of residue as distillation proceeds.

Rheological Temperature Susceptibilities

These susceptibilities were determined as penetration indices(2) from penetrations taken from 4°C to 40°C. The equation used to calculate the penetration index is given as:

$$PI=(20-500A)/(50A+1) \qquad 1)$$

where A is the slope obtained from the plot of logarithm (base 10) of the penetration in dmm with temperature in centigrade degrees.

Blending

The final distillation residue [+533°C] was blended with calculated amounts of the distillates to simulate the residues obtained when the distillation cuts were made. These blends and the blends obtained with other materials were thoroughly mixed at 135°C -150°C.

Blending Materials

Biomass Derived Oil (BDO)- This is a highly polar material, topped at 350°C, whose major functional groups consist largely of amides. It has nitrogen and oxygen contents of 4 wt % and 6 wt % respectively.

Mineral Oil (Min)- This oil was purchased from Fisher Scientific and consists of high boiling saturated hydrocarbons.

Hydrogenated Syncrude Gas Oil (H2Syn)- This gas oil consists predominantly of saturated aliphatic and naphthenic hydrocarbons with some aromatic hydrocarbons.

Waste Banbury Oil (Ban)- This high boiling oil is highly naphthenic and was used in the processing of rubber. It was obtained from Trent Rubber Services Inc.

Dutrex 776™ (Dut)- This Shell Oil product has a saturated hydrocarbon content of 24.4%, naphthenic-aromatics of 63.3% and polar components of 12.0%. It distils between 375°C and 580°C.

Shale Oil (Shale)- This was produced from New Brunswick oil sh le. These shale oils are known to have high contents of nitrogenous components.

Paraffinic Gas Oil (Para)- This was obtained from a waxy conventional crude oil.

Results and Discussion

The effect of distillation on the rheological temperature susceptibilities that are expressed in terms of "Penetration Index" (PI) are shown in Fig. 3, 4 and 5. As the distillation proceeds the PI of the residues increases. Also, the saturated hydrocarbon content of the distillates decreases and the polar components increase as shown in Table 1. Since the PI increases as materials are removed by distillation, it seems that components that are undesirable for low temperature susceptibility are being removed.

It is assumed that most of the distillate obtained from the Cold Lake asphalt originated from the continuous phase or uncomplexed material according to the model proposed earlier. Therefore, it would be expected that this phase became smaller as distillation proceeded. As there are temperature dependent equilibria of exchangeable components between the continuous and complexed phases and since the continuous phase decreases there should be a trend for the exchangeable components, in particular the more highly polar ones, to be forced into the complexes. This would leave a new fraction of less polar components in the exchangeable state which could be more responsive to temperature changes and result in greater resistance to viscosity changes. Also, the distillation changes the composition of the continuous phase (Table 1) and thereby changes the affinity of this phase for exchangeable components which favours greater responses to temperature changes.

Figure 5 plots PI vs the penetrations at 25°C of the various blends. The initial blends are designated by the suffix 1 and the subsequent blends designated by the suffix 2, i.e., Min1 and Min2. The curve on this plot represents the Cold Lake residues obtained during distillation and is used as a curve of reference in the subsequent figures.

As shown in Fig. 6, when the highly polar biomass derived oil (5%) was blended with the +533°C residue the PI fell below that of the reference curve indicating that highly polar components are not desirable. This blend probably is quite complex, because some of the polar components of this oil might displace some of the original asphalt polar components from the micelles or complexes. The balance of affinities of the two phases for the interchangeable components becomes less favourable for resisting viscosity changes with changing temperatures. Therefore, it could be argued that the increase in PI during distillation is due to some decrease in undesired polar components.

The blend containing the first addition [5%] of the hydrogenated Syncrude (H2Syn1) had the highest PI, followed by that containing a similar amount of Banbury oil (Ban1) then that containing about 10% Dutrex (Dut1). A blend that contained a similar amount of mineral oil (Min1) and 10% of paraffinic oil (Para1) also had improved PI and the 5% shale oil blend (Shale1) can be considered neutral.

These trends change dramatically when twice the initial amount of these blending agents is added. The PI decreased in the blends containing Syncrude (H2Syn2), the Dutrex (Dut2) and paraffin (Para2). The PI of the Syncrude (H2Syn2) decreased by approximately 1.5 PI units. The PI of the Banbury oil blend (Ban2) also decreased, but still remains fairly high. The PI of the shale oil blend (Shale2), which was about the same as the +533°C residue, only decreased by as much as the reference curve during the increase in penetration. Therefore, it can be considered neutral again. It is quite remarkable that the PI of the blend containing the increased amount of mineral oil increased marginally.

When another increment of the mineral oil (13.26%) was added as shown in Fig. 7, a moderate decrease in the PI occurred due to an upset in the ratio of saturated hydrocarbon to aromatic plus naphthenic components. As shown in Fig. 8, when small amounts of the Syncrude gas oil were added to the mineral oil [~9%] containing blend, it appeared to have little effect. However, when added to a blend containing a larger amount there was significant positive effect, but when more was added the PI decreased although with the increased softening, this decrease was similar to that in the reference curve. Similar results were obtained when Banbury oil was added to blends containing the mineral oil as shown in Fig. 9. In this case, a blend had a penetration similar to the starting Cold Lake asphalt but with a PI about 1.5 PI units higher.

It appears that replacing the distillates from the Cold Lake asphalt with the various blending agents modified the continuous phase and this affected the responses to temperature changes.

Conclusions

It has been shown that the composition of the distillable portion of asphalt can have a major effect on temperature susceptibility. Also, it has been shown that for Cold Lake asphalt, blending can increase the PI by at least 1.5 units. These effects can be explained on the basis of a proposed model. Work is continuing on the quantification of the model.

References

1. Sawatzky, H., Farnand, B., Houde, J. Jr. and Clelland, I., Div. of Petrol. Chem., ACS, Aug, 1992.

2. Pfeiffer, J.P. and van Doormaal, P.M., J. Inst. Petrol. Technol., 22, 414 (1936).

Table 1 - Component types in distillation fractions (%)*

	350 °C -448 °C	449 °C -482 °C	483 °C -497 °C	498 °C -529 °C	530 °C -533 °C
Saturates	34.4, 34.2	29.55, 29.86	28.04, 31.36	22.63, 22.91	18.58, 18.98, 19.81
avg.:	34.3	29.7	29.7	22.8	19.1
Naphthene-Aromatics I	27.78, 38.24	39.92, 40.79	43.30, 31.09	46.31, 41.08	41.90, 28.05, 29.85
avg.:	33.0	39.9	37.2	43.6	32.3
Naphthene-Aromatics II	27.28, 14.32	19.88, 17.91	16.08, 20.51	15.61, 21.21	16.82, 26.64, 31.23
avg.:	20.8	18.9	18.3	18.4	24.9
Polar Aromatics	5.75, 8.32	6.99, 7.53	9.21, 13.26	10.58, 10.87	13.78, 17.14, 10.67
avg.:	7.0	7.2	11.2	10.8	13.9
Loss	7.80, 4.91	3.67, 3.91	3.39, 3.78	4.87, 3.93	8.92, 9.19, 8.44
avg.:	4.9	3.8	3.6	4.4	8.9

* Modified ASTM D4124 procedure scaled down by a factor of 10.

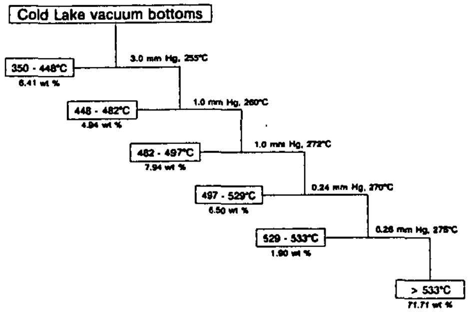

Fig 1 - Conditions and yields of vacuum distillation of Cold Lake vacuum bottoms

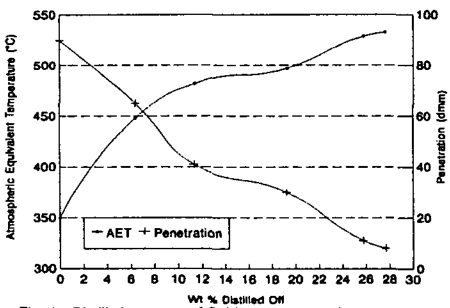

Fig. 2 - Distillation curve of Cold Lake vacuum bottoms and change in penetration of residue as distillation proceeds

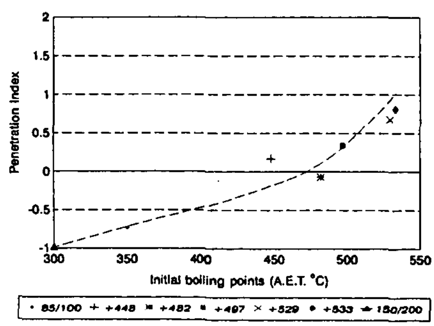

Fig. 3 - Penetration index vs Cold Lake vacuum bottoms 47-CL-89

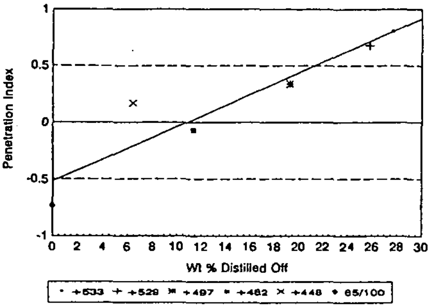

Fig. 4 - Penetration index vs wt % distilled off of Cold Lake vacuum bottoms

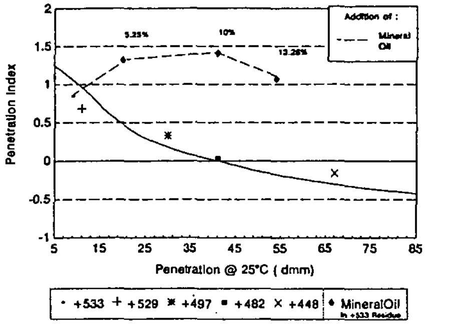

Fig. 7 - Penetration index vs penetration at 25°C of Cold Lake vacuum bottom blends

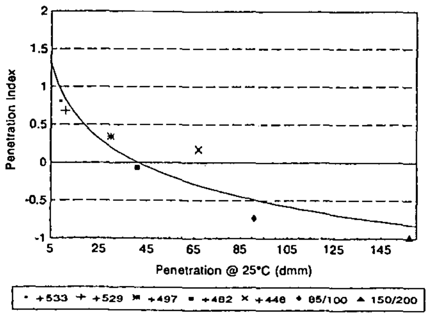

Fig. 5 - Penetration index vs penetration at 25°C of Cold Lake vacuum bottoms

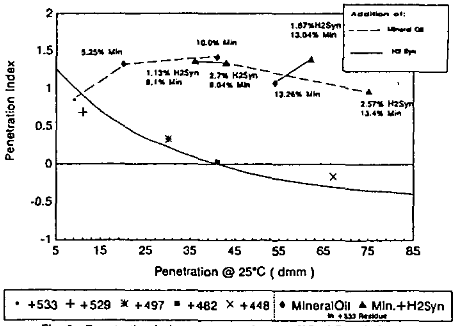

Fig. 8 - Penetration index vs penetration at 25°C of Cold Lake vacuum bottom blends

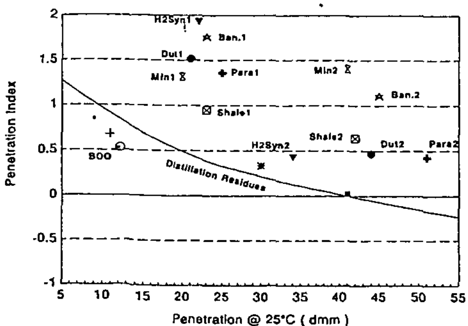

Fig. 6 - Penetration index vs penetration at 25°C of +533°C Cold Lake vacuum bottom blends

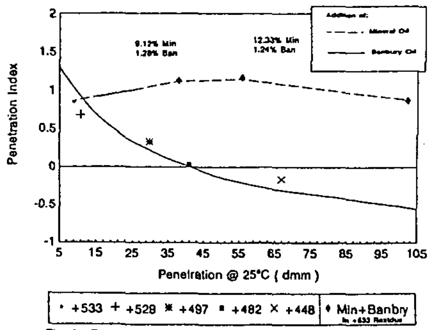

Fig. 9 - Penetration index vs penetration at 25°C of Cold Lake vacuum bottom blends